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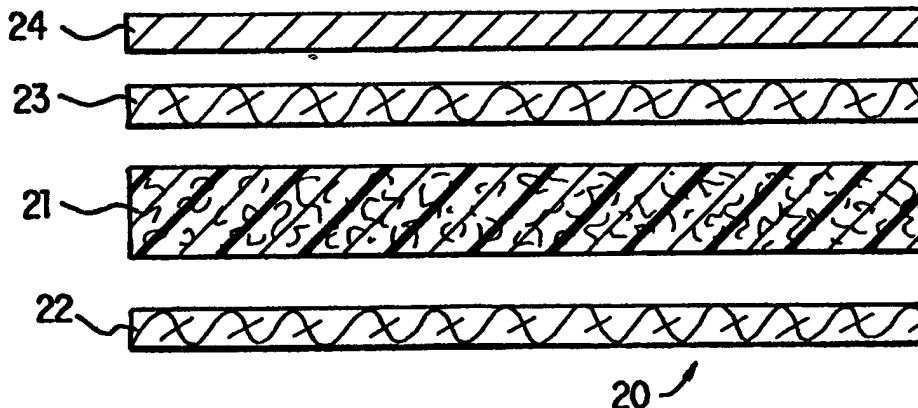
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(54) Title: PROCESS OF MAKING A PRINTED WIRING BOARD CORE STOCK AND PRODUCT FORMED THEREFROM



(57) Abstract

Process provides wetlaid printed wiring board core stock precursor material that incorporates resin within cellulose matrix and that can be partially cured by conventional means to form PWB B-stage materials (20). Process also provides for reducing dielectric constant and dissipation factor of a PWB core stock and of PWB composite material made therefrom, by incorporating material having dielectric constant lower than that of cellulose fibers directly into cellulose matrix forming the core stock (21). Among materials that can be incorporated into cellulose matrix are fibrous materials, including glass fibers (23) and/or synthetic fibers, and/or particulate constituents such as glass microspheres, glass beads, glass shot, aramid fibers, aramid powders, ceramic microspheres, and clay. Other additives, such as flame retardants, may also be incorporated into novel paperboard materials of the invention.

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PROCESS OF MAKING A PRINTED WIRING BOARD CORE STOCK AND PRODUCT FORMED THEREFROM

This invention relates to the manufacture of printed wiring board core stock material that comprises a resin system formed within a fibrous matrix. The printed wiring board core stock material may be produced with functional fillers dispersed within its fibrous matrix.

Background of Invention and Prior Art

Laminates for forming printed wiring board ("PWB", also known as printed circuit board) generally comprise at least one conductive layer and at least one support layer. The conductive layer is often formed from a thin sheet of copper. The support layer is often formed from a paper or a fiberglass sheet that has been impregnated with a solvent-based resin system. Six important grades or types of PWB laminate are designated CEM-1, CEM-3, FR-1, FR-2, FR-3, and FR-4. CEM-1 support layers are generally formed of paper that is impregnated with a solvent-based epoxy resin system. CEM-3 support layers are generally formed of nonwoven glass material that is impregnated with a solvent-based epoxy resin system. FR-1, FR-2, and FR-3 support layers are generally formed of paper impregnated with a solvent-based phenolic resin system. FR-4 support layers are generally formed of fiberglass sheet impregnated with a solvent-based epoxy resin system.

Following impregnation, the support layers are generally dried to partially polymerize the resins, forming materials known in the industry as "B-stage" materials. The semi-cured resin in or on a substrate is also known as a "prepreg". The prepreg is dry and non-tacky. It can be rolled and sold as is or cut into sheets for further processing. The B-stage materials are collated with other laminate components including a conductive layer and then processed on production equipment to form the "C-stage" (that is, fully cured) PWB material.

As more and more electronic components are added to the PWB, the functional significance of the dielectric properties of the core layer has grown. With closely spaced electronic components and higher frequency electronics, it is desirable that the dielectric constant of the core layer be decreased, in order to

prevent transmission of electrical occurrences between adjacent electrical components (that is, to prevent "cross talk"). Cellulose fibers as well as the resins generally used to form B-stage materials do have relatively low dielectric constants. However, as will be seen herein, lower dielectric constants are achievable with the
5 addition of functional fillers and fibers in the described process.

Typically, paper for PWB core stock is produced on a fourdrinier paper machine and is subsequently impregnated with epoxy resin that has been dissolved in organic solvents. Multiple layers of this material are laminated together to form the core paperboard used in the final PWB manufacturing process, adding additional
10 process variables and expense with each additional layer.

Many different approaches have been followed in making printed circuit board composites. Some examples thereof may be found in U.S. Patents Nos. 4,879,164; 4,562,119; 4,518,646; and 3,895,158.

Cellulose matrix materials comprising, in various amounts, resin components
15 and components such as microspheres, have been developed for a variety of applications.

U. S. Patent No. 5,272,006 claims a matrix mold used in the manufacture of flexographic printing plates. The mold comprises a matrix board including 5% to 20% fibers, 25% to 40% resin binder, and 50% to 65% fillers.

20 U. S. Patent No. 4,379,808 discloses a process for making paperboard sheet on a cylinder board machine. The Example describes an embodiment comprising 65% cellulose fibers, 15% polypropylene resin, and 20% talc. The field of the invention of the '808 patent is forming board sheet for use in making structural materials, packaging materials, etc.

25 U.S. Patent No. 4,137,363 discloses matrix materials that comprise from 22.28% (Ex. 3) to 26.52% (Ex. 4) cellulose material, from 36.15% (Ex. 5) to 39.59% (Ex 1) resin plus cross-linker, from 4.91% (Ex. 1) to 12.80% (Ex. 5) glass "microbubbles", from 0.40% (Ex. 3) to 0.68% (Ex. 4) miscellaneous materials, and from 36.15% (Ex. 5) to 39.59% (Ex. 1) asbestos. The matrix materials of the '363
30 patent are taught to be useful for forming molds that are in turn used in the formation of flexographic printing plates.

U.S. Patent No. 4,133,688 discloses matrix materials that comprise cellulose and, with reference to the cellulose, 0.5% alkylketene dimer, 1% polyamide/

polyamine-epichlorohydrin resin, and 1% vinylidene chloride/acrylonitrile microspheres (Ex. 1) or 0.5% color photo resin glue, 0.7% sodium stearate, 2% vinylidene chloride/acrylonitrile microspheres, and aluminum sulfate to reduce the pH to 4.5 (Ex. 3). The matrix materials of the '688 patent are taught to be useful as
5 photographic papers.

Objects and Summary of Invention

It is one object of this invention to provide a process for the manufacture of
10 fibrous printed wiring board core stock material. which process does not require a resin-impregnation step. The process of this invention may be varied both as to kinds and relative amounts of materials used and as to processing parameters that can be employed.

It is another object of this invention to provide a process for the manufacture
15 of cellulose PWB core stock that incorporates a resin system into the core stock prior to forming the core stock.

It is yet another object of this invention to provide sheets of cellulose PWB core stock that are manufactured in a thickness suitable for use as the entire core stock element, without the necessity of lamination to build core stock thickness, in
20 the manufacture of printed wiring board.

It is still another object of this invention to provide cellulose PWB core stock having improved dielectric properties.

The present invention provides an improved process for the manufacture of PWB B-stage core stock. The process is improved in that it avoids the necessity for
25 impregnation of a substrate with a resin solution, as is commonly done in conventional processes. The process provides core stock precursor material that incorporates resin within a cellulose matrix and that can be partially cured by conventional means to form PWB B-stage materials.

The present invention also provides for improving (reducing) the dielectric
30 constant and dissipation factor of a PWB core stock, and hence of a PWB composite made therefrom. This improvement is accomplished by incorporating a material having a dielectric constant lower than that of the cellulose fibers directly into a cellulose matrix forming the core stock. Among the materials that can be

incorporated into cellulose matrices in accordance with the present invention are fibrous materials including glass fibers, synthetic fibers, aramid fibers, or a blend of glass and synthetic fibers, especially those with very low dielectric fibers such as E-glass, and ceramic fibers. Alternatively, the present invention contemplates the
5 incorporation of particulate constituents that range in size from about 0.2 to about 20 micrometers in diameter, such as glass microspheres, glass beads, glass shot, aramid powders, ceramic microspheres, and clay.

The present invention provides a process for the manufacture of printed wiring board core stock material that comprises the steps of forming a dispersion of
10 cellulose fibers in water, adding a resin system comprising epoxy resin monomer and curing agent, in stoichiometric ratio, to the dispersion of cellulose fibers to form an aqueous mixture comprising a solids content of from about 65 weight-% to about 25 weight-% of cellulose fibers and from about 35 weight-% to about 75 weight-% of the resin system, and forming the mixture into a paperboard sheet. Preferably, the
15 curing agent is retained within the paperboard sheet and the curing agent reacts substantially completely to cross-link the epoxy resin monomer when the paperboard sheet is maintained at a temperature of approximately 340°F for 30-60 minutes. A preferred curing agent is dicyandiamide. When the curing agent is an amine, a neutralizing agent is added to the mixture of resin system and cellulose fibers to
20 reduce the pH thereof to neutral or slightly acidic. An amine curing agent herein preferably has a number average molecular weight of at least 100 and an amine functionality of at least 3.

Functional additives — preferably glass fibers, aramid fibers, aramid powders, glass microbubbles, ceramic fibers, ceramic microbubbles, and/or clay — having
25 dielectric constants and dissipation factors lower than that of the cellulose fibers, can be added to the dispersion of cellulose fibers in water. Other additives may also be incorporated into the novel paperboard materials of the present invention. For instance, it is very often desirable to incorporate flame retardants therein.

The process of the invention further contemplates drying the paperboard
30 sheet without substantial cross-linking of the epoxy resin monomers and calendering the dried paperboard so-formed to form B-stage printed wiring board core stock material.

This invention provides printed wiring board core stock material comprising from about 25 weight-% to about 65 weight-% cellulose fibers forming a cellulose matrix, and having substantially evenly distributed throughout the matrix from about 75 weight-% to about 35 weight-% of a resin system comprising an epoxy resin and a curing agent. The cellulose fibers can comprise a mixture of softwood and hardwood fibers. The resin system can comprise components that are brominated to a degree sufficient to impart flame retardant properties to said core stock material. This invention provides printed wiring board core stock material comprising from about 25 weight-% to about 65 weight-% cellulose fibers, from about 75 weight-% to about 35 weight-% of a resin system comprising an epoxy resin and a curing agent, and from about 2 weight-% to about 20 weight-% of a functional additive having a dielectric constant and dissipation factor lower than that of the cellulose fibers.

Specific embodiments of the present invention include printed wiring board core stock material comprising about 15 weight-% softwood fibers, about 12 weight-% hardwood fibers, about 63 weight-% of a resin system, and about 7 weight-% silane-coated calcined kaolin and also material comprising about 20 weight-% softwood fibers, about 16 weight-% hardwood fibers, about 56 weight-% of a resin system, about 4 weight-% glass fibers, and about 6 weight-% silane-coated calcined kaolin. A preferred embodiment comprises about 26 weight-% softwood fibers, about 8½ weight-% hardwood fibers, about 5 weight-% glass fibers, about 55 weight-% of a resin system, and about 5½ weight-% antimony trioxide. Still another preferred embodiment comprises about 23 weight-% softwood fibers, about 8 weight-% hardwood fibers, about 57 weight-% of a resin system comprising an epoxy resin and a dicyandiamide curing agent, about 4.5 weight-% glass fibers, about 4.5 weight-% glass microspheres, and about 3 weight-% antimony trioxide.

Several other specific embodiments of the printed wiring board core stock material of the present invention are disclosed below, and many, many more will be apparent to those skilled in the art based upon the disclosure herein.

The present invention includes the products of each of the processes disclosed herein, and further includes printed wiring board composites that comprise a core formed of core stock material as defined herein. While paperboard sheets made in accordance with the present invention are particularly useful in the

manufacture of printed wiring board, they can also be used for other purposes such as in the manufacture of gaskets and of molded three-dimensional objects.

Brief Description of the Drawings

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This invention is described and explained in more detail below using certain embodiments illustrated in the drawings. The described and drawn features, in other embodiments of the invention, can be used individually or in combination. The drawings are not necessarily to scale, emphasis instead being placed upon the illustration of principles of the invention in a clear manner.

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Figure 1 is a schematic illustration of one type of machine that can be used to make PWB core stock material in accordance with this invention;

Figure 2a is a schematic view of an assembly of sheets constituting a make-up for a PWB laminate; and

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Figure 2b is a cross-sectional view of a unitary consolidated PWB laminate in accordance with one aspect of this invention.

Description of Preferred Embodiments

20

CELLULOSE MATERIALS. For most applications cellulose fibers derived from wood pulp are the most economical source for the cellulose matrix of the present invention. Cellulose fibers from other sources such as cotton would also function in accordance with the principles of this invention.

25

Wood consists of cellulose fiber and a substance called lignin which holds them together. Wood pulps consist mostly of cellulose fibers that have been separated from each other by chemical, mechanical, and/or thermal processing that removes or destroys, at least partially, the lignin that holds the cellulose fibers together. Wood pulp is produced as sheets of loosely cohered cellulose fibers containing a minor proportion of water. In use, the wood pulp sheets are generally broken up and dispersed in a large quantity of water (e.g., to a consistency of 1 weight-% or less).

30

In accordance with the present invention, cellulose fibers provide a reinforcing network or web structure (matrix) within which epoxy resin material and optionally

functional additive is distributed. The cellulose fibers enhance ductile and tensile properties of the cellulose matrix material incorporating them. Both softwood (e.g., spruce) and hardwood (e.g., birch) fibers may be used alone or may be blended to produce the cellulose matrix. Softwood fibers are generally about 4 mm. in length, while hardwood fibers are generally about 1.4 mm. long. In general, paper or paperboard made with softwood fibers will have good flexibility and tear strength, whereas those made with hardwood fibers will have good tensile strength and dimensional stability. By choosing a suitable combination of softwood and hardwood fibers, one can tailor the properties of the ultimate PWB core stock produced. It has been found that the majority of hardwood matrices tend to resist resin flow more than do softwood matrices. Accordingly, matrices that are rich in hardwood fibers will generally take more resin than similar matrices rich in softwood fibers. However, there are a few hardwood fibers that aid in paper formation, and these hardwoods do not hinder resin flow. Accordingly, a percentage of hardwood, up to 25 weight-%, is beneficial in this process.

The demands of the application require that PWB core stock material be extremely uniform in thickness and density. To achieve this, the wood fibers must be distributed quite uniformly throughout the sheet during the papermaking process. Uniform fiber distribution in a sheet is referred to as good "formation". Formation is generally dependent upon two initial mechanical considerations in the stock preparation phase – degree of dispersion and degree of refining. Dispersion is the separation of fibers by mechanical mixing in water. Refining is the physical alteration of fibers caused by shearing them in wet slurry form between two opposing media such as rotating ridged steel disks. In a most preferred embodiment of the present invention, softwood/hardwood pulp combinations are dispersed in water in a tank-agitator system called a slusher. The concentration of fiber in the water is 0.5 weight-% bone dry solids (0.5 weight-% bone dry consistency). The fibers are dispersed until no fiber bundles appear in a visual inspection of an extremely dilute sample. After dispersion, the pulp slurry is refined in a rotary-ridged-roll-and-tank system (laboratory) or in a conical or disk refiner (production). Refining is controlled by measuring the drainage rate for the water in the pulp slurry. Refining fibers for use in this invention may be carried out to drainage rates in the range of 50-700 ml. as measured by the Canadian Standard Freeness test. Fiber dispersions with the

lower CSF values improve retention of the stock and reduce loss of powdered resin during the manufacturing process.

Another aspect of the cellulose matrix that is important to the manufacture of PWB core stock is porosity. The matrix materials and other components should be selected so as to minimize porosity in the core stock, because pores therein are likely to trap moisture and resist resin flow, which will result in dielectric breakdown.

RESIN SYSTEMS. A resin system of the present invention comprises two aspects: monomer and cross-linker (or "curing agent").

The monomer is preferably a diglycidyl ether of bisphenol A. Such monomers form what are known as "epoxy" resins. The monomers may be formed by reacting epichlorohydrin and bisphenol A. An epoxide group at both ends of the monomer provides the reactive chemistry of the resin. In order to generate an epoxy resin suitable for the present invention, this monomer may be upstaged by reaction with tetrabromobisphenol A to yield a flame-retardant resin. This synthetic reaction produces a mixture of oligomers with a molecular weight distribution of 100-3000 epoxide equivalent weight (EEW). Low EEW resins generally result in a rigid laminate while high EEW ones lead to more flexible properties. Flame retardant properties can also be imparted to a resin system by the incorporation therein of flame retardant additives and fillers such as brominated diphenyl ether, zinc borate, antimony trioxide, and aluminum trihydrate.

Polyester resin monomers, cyanate ester resin monomers, polyimide resin monomers, and blends of bismaleimide/triazine with difunctional epoxy monomers may be incorporated into CEM-1 core stock material in accordance with the present invention. The resin system may also contain multifunctional additives such as tetrafunctional epoxy resins, epoxy phenol novolaks, epoxy cresol novolaks, epoxy p-aminophenol, and epoxy isocyanurate to improve the cross-link density of the cured matrix. Higher cross-link density improves such properties of the core stock material as glass transition temperature, chemical resistance, z-axis expansion, and/or thermal shock resistance.

Epoxy resins that can be used in accordance with the present invention include the following:

EPI-REZ 3522-W-60 is a nonionic aqueous dispersion of a solid bisphenol A epoxy resin with an epoxide equivalent weight of 550-650 and a Durrans' melting point of 75-85°C. It contains no organic solvents. This resin is supplied at a moderate viscosity and is mechanically stable. It is available from Shell

5 Chemical Company of Houston, Texas.

PEP-6007 WPM-55 is a nonionic aqueous dispersion of a solid bisphenol A epoxy resin with an epoxide equivalent weight of 1800. It is supplied at 55 weight-% solids in water and propylene glycol monomethyl ether. It can be cross-linked with urea, melamine, and/or formaldehyde resins and/or phenolic-type resins. It is available from Pacific Epoxy Polymers, Inc. of Richmond, Missouri. Similar materials are available from other manufacturers.

10 ARALDITE PZ-3907 is a nonionic aqueous dispersion of a high molecular weight epoxy resin with an epoxide equivalent weight of 1760-2200. It is supplied at 55 weight-% solids in water and 2-propoxyethanol. It can be used to form one-component or two-component heat-cured systems with carboxyl-containing acrylics, melamine, urea, and/or formaldehyde resins and/or phenolic-type resins. It is available from Ciba Specialty Chemicals of Brewster, New York.

15 EPON Resin 2002 is a solid bisphenol A/epichlorohydrin epoxy resin with an epoxide equivalent weight of 675-760. It provides controlled and extended gelation time in epoxy powder coatings to maximize flow and leveling. It is available from Shell Chemical Company. Similar materials are available from other sources such as Dow Chemical Company of Midland, Michigan (D.E.R. 662UH) and Ciba Specialty Chemicals (GT 6063).

20 EPON Resin 2005 is a fusion-derived solid bisphenol A/epichlorohydrin epoxy resin with an epoxide equivalent weight of 1200-1400. It is low in moisture and total volatile content. It provides consistent cure response with a wide variety of curing agents. It is available from Shell Chemical Company.

25 EPON Resin 2042 is a modified bisphenol A solid resin. It has a very low viscosity with a high softening point. It is especially beneficial in mixed resin systems because of its low melt viscosity. It is available from Shell Chemical Company.

30 EPON Resin 1183 is a solid brominated epoxy resin with a 42 weight-% by weight bromine content and an epoxide equivalent weight of about 670. It is

designed for applications requiring good sintering resistance at room temperature and moderate flammability resistance. It offers alternatives to tetrabromobisphenol A, octa- and decabromodiphenyl oxides, antimony trioxide, phosphorus compounds, and other flame-retardant additives for a variety of applications. It is available from Shell Chemical Company. Similar materials are available from other sources such as Dow Chemical Company (D.E.R. 542) and Ciba Specialty Chemicals (LT 8049).

EPON Resin DX-5114 is a non-sintering solid brominated epoxy resin with a 51 weight-% by weight bromine content and an epoxide equivalent weight of about 715 and a Durrans' melting point of 105°C. It is designed to be melt-blended with thermoplastic polymers or epoxy resins to produce materials that are flame-retardant. It is available from Shell Chemical Company.

In general, epoxy resins can be cured using many different hardeners. Selection of the optimum curing agent for a particular application is governed by application techniques, pot life requirements, cure conditions, and desired physical properties. Curing agents affect the viscosity and reactivity of the formulation and determine the type of chemical bond, cross-link density, and thereafter the final properties of the cured formulation. Among them are: anhydrides, such as trimellitic anhydride; dicyandiamide (DICY) and DICY-like chemicals; polyamides, such as Versamide; formaldehydes, such as melamine/formaldehydes, urea/formaldehydes, and phenol/formaldehydes, including resole and novolak; and amines. For the present invention, it has been discovered that the anhydrides are unsuitable because of their sensitivity to water. Polyamides do not work well because the cured formulation has very poor thermal properties at high application temperature. The formaldehyde curing agents have been found to be unsuitable because they are not B-stageable. Direct application of dicyandiamide is not desirable because it causes unacceptable contamination of waste water. Amines are the curing agents of choice for direct application in the present invention. Particularly suitable are polyfunctional amines that are soluble in water and that are retained in the wet web of the composite during the core stock boardmaking process. Dicyandiamide and like materials can be melt-compounded into the resin system when it is desired to use a powdered resin system.

Many different types of curing agents can be used in this invention. Curing agents that have been found to be useful in accordance with the present invention include the following:

5 XJT-504 has a functionality of 4 and a molecular weight of about 148. It is a fast-reacting polyetherdiamine with characteristic flexibilizing and toughening properties. Epoxy resins cured with this curing agent can be formulated to cure rapidly at elevated temperature. It is available from Huntsman Petrochemical Corporation of Houston, Texas.

10 EPI-CURE P101 is a chemically stable, low bake or ultra-rapid curing, epoxy powder coating converter. It takes the form of a free-flowing pulverized amine adduct. It is compatible with epoxy resins when extruded or hot-melt mixed therewith, and provides a homogeneous blend of epoxy resin and curing agent. It can be incorporated as a curing agent with EPON Resin 2002 at 2 parts by weight by 100 parts by weight of epoxy resin. It is available from Shell Chemical
15 Company.

EPI-CURE P108 is an accelerated dicyandiamide curative used for high performance decorative powder coatings. It is quite compatible with laminating and curing processes currently used in the PWB industry, and is available from Shell Chemical Company. Similar materials are available from Ciba Specialty
20 Chemicals (HT 2844).

All ingredients can be added to the pulper individually. Alternatively, powdered resin systems for use in this invention can conveniently be made by the melt-compounding processes. The ingredients (resin, curative, and if desired
25 functional filler) are mixed together, melted, and uniformly blended at elevated temperature. They are then cooled, crushed, ground, and sifted. Stoichiometric ratios of resin systems prepared in this way are uniform to the microscopic level, regardless of the percentage retained in the cellulose matrix during PWB core stock manufacturing processes.

30 Resin systems for use in this invention will preferably show minimum curing activity at up to about 240°F but will be fully cured by being heated at about 340°F for about 30-60 minutes. The resin system can be modified to cure at different temperatures and different time periods, in order to meet changes that occur in this

or other industries. Additionally, it is beneficial if the resin systems have gel times longer than about 2½ minutes at about 260-300°F and have minimum viscosity at their melting points. The subject material is termed "B-staged" when the uncured resin is incorporated within the board matrix, but the board has not been raised to the curing temperature for a period of time sufficient to cure it.

One typical resin system of this invention comprises 86 weight-% EPON Resin 2002, 10 weight-% brominated diphenyl ether, and 4 weight-% EPI-CURE P108. This resin system is referred to as Ly-Resin 4. Another typical resin system of this invention comprises 48 weight-% EPON Resin 2002, 48 weight-% EPON Resin 1183, and 4 weight-% EPI-CURE P108. This resin system, which contains 21 weight-% bromine, is referred to as Ly-Resin 5. Both Ly-Resin 4 and Ly-Resin 5 were tested alone and met UL 94V0 flame retardant requirements.

FUNCTIONAL FILLERS. A prime objective of the fillers which are incorporated into the fibrous matrix materials of the present invention is to improve the electrical, mechanical, and thermal properties of the matrices. Another objective of the fillers is to improve the flame retardant properties of the matrices. An additional benefit is that many of these fillers actually promote even distribution of the resin components within the matrices.

One excellent filler choice is Translink 445, a calcined kaolin clay surface-treated with amino-silane, provided by Engelhard Corporation of Edison, New Jersey. Translink 445 is cure-compatible with epoxy resins. Its average particle size is about 1.4 microns. It reduces water/moisture absorption, increases tensile and flexural strength, increases heat deformation temperature, increases dimensional stability, and improves high speed/high frequency performance.

Another suitable class of functional fillers is microspheres or microbubbles. For instance, one can incorporate into the fibrous matrices from 1½ weight-% to 15 weight-% of Eccospheres SI glass microballoons from Emerson & Cuming, Inc. of Canton, Massachusetts. The SI microballoons are high silica glass, hollow, thin-walled spheres, ranging in diameter from 5 to 150 microns. Their dielectric constant in the frequency range from 1 MHz to 8.6 GHz is about 1.2, and their dissipation factor in the same frequency range is only 0.0005. Another example of such materials are Scotchlite K46 glass microspheres available from Minnesota Mining &

Manufacturing, Inc. of St. Paul, Minnesota. They range up to 80 microns in diameter.

Glass fiber can also contribute a reinforcing fibrous network in the matrix, as well as enhancing dimensional stability and electrical properties. Glass fibers used in the invention in low percentages provide a bridging network for resin flow and provide improved electrical properties. One example of suitable glass fiber is Evanite microfiber 411 ("B-glass"), provided by Evanite Fiber Corporation of Corvallis, Oregon. Its average fiber diameter is about 3 microns. Another suitable glass fiber is PPG Type 3156, a chopped strand electric grade (or "E-glass") fiber of 10 micron diameter. PPG Type 3156 is provided by PPG Industries, Inc. of Warrington, Pennsylvania, coated with a PPG-propriety silane-based finish that maximizes epoxy resin wet-out and flow during manufacture of cellulose matrix materials of the present invention. Owens-Corning fiberglass materials, as well as similar materials produced by other manufacturers, would also be suitable for this application. In addition to glass fibers, synthetic fibers can also supply the bridging network, improved electrical properties, and resin flow permeability that make synthetic fiber useful. Suitable synthetic fibers include nylons, polyolefins, polyesters, aramids, and the like.

Flame retardant chemicals can also be used as fillers in the present invention. Among the suitable chemicals are halogenated compounds, such as decabromodiphenyl oxide, and synergist compositions such as antimony trioxide and zinc borate, as well as combinations of such compounds and compositions. An example of a suitable decabromodiphenyl oxide is DE-83R, available from Great Lakes Chemical Corporation of West Lafayette, Indiana. Antimony trioxide can be obtained from Total Specialty Chemicals Inc. of Norwalk, Connecticut. Zinc borate can be obtained from U.S. Borax Inc. of Valencia, California.

BOARDMAKING

Stock preparation. Sheets of wood pulp are dispersed in water in a mixing tank known as a pulper. While any type of wood pulp, or indeed any source of cellulose fibers suitable for papermaking, can be used, especially good results have

been achieved with a blend of softwood and hardwood pulps in a ratio of from 1:1 to 1.33:1.

Mechanical action of the pulper disperses the dry compacted pulp fibers into an even suspension known as a stock slurry or simply stock. The percent solids in the stock (percent consistency) can range from 0.4% to 8% by weight. The dispersion of the stock is monitored visually by placing a small amount of it in a transparent container and diluting it until individual fibers can be distinguished from fiber bundles in the stock. The stock is said to be fully dispersed when no fiber bundles are visible.

A refining process is used to control various parameters including stock drainage rate on the paper former, paper formation, and paper physical properties such as web strength, stiffness, density, and porosity. Refining is accomplished by mechanical action carried out on the fiber slurry when it is passed between two rotating, close-gapped, opposing surfaces, such as nested-cone or twin-disk refiners. The surfaces of these devices are covered with raised bar patterns that produce the shear force required to peel small fibrils partially away from the surface of the main fiber; this process is known as fibrillation. Fibrils greatly increase the surface area and potential contact or bonding sites on the cellulose fibers, thus enhancing the strength of the paper web. Specific response to refining is a function of particular equipment used, fiber type, and operating conditions. Degree of refining is monitored by noting the rate at which water drains from a suspension of fibers through a wire mesh on which a paper sheet is being formed. Drainage rate is measured in terms of Canadian Standard Freeness (CSF). This is a procedure for measuring the drainage rate of a suspension of 3 grams of fibrous material in 1 liter of water. Measurement and apparatus are according to TAPPI Standard T227 m-58. Results are reported as volume in milliliters of water drained under standard conditions. The measured value is affected by the fineness and flexibility of the fibers and by their degree of fibrillation. The greater the refining action, the slower the water drains from the sheet.

Tear strength generally decreases with refining due to loss of strength by the individual fibers. Other strength parameters such as burst strength and tensile strength increase due to improved fiber-to-fiber bonding. As the paper stock becomes slower, that is, more difficult to drain, the paper becomes denser, with

reduced porosity. A CSF of about 200 has been found to be suitable in the practice of the present invention. However, this value is not critical, and may be varied widely.

Once the pulp reaches the desired degree of freeness, the stock is pumped
5 back to the pulper. Dry resin systems and functional fillers are added and the resulting mixture is pulped until those additives are fully dispersed. The stock is then pumped to a mixing tank, where – if desired – waterborne resins and liquid curing agents can be added. The mixing tank is equipped with a gentle agitator whose speed can be controlled and adjusted. Once thorough mixing is achieved, the pH of
10 the stock is measured. When this invention uses amine curing agents, the stock is usually alkaline (pH = 9½-10). Alum or another neutralizing agent is added to reduce the pH of the mixture to the range 6-8. The stock is then pumped to the machine chest.

15 Formation. Prepared stock is pumped from a machine storage chest to a headbox, which is connected to a papermaking machine, such as that described herein below. The function of the headbox (or flowbox) is to take stock delivered by a fan pump and to transform its flow into an even, rectangular discharge across the width of the paper machine. If foam is generated during the wet operation, a
20 defoamer diluted with water to a low concentration, for instance Amergel 200 diluted to 5% by weight, may be fed into the headbox.

A precipitating agent in a dilute solution, for instance Nalco 7524 paper process polymer at 0.25% by weight in water, is fed into the headbox. Nalco 7524 is a high molecular weight, highly charged, cationic copolymer in liquid emulsion. It is
25 available from Nalco Chemical Company of Naperville, Illinois. Due to an interaction between the precipitating agent and the prepared stock, the various materials in the stock will be flocculated and fine particles of the stock materials will attach to larger particles. This flocculation significantly increases the retention of all of the raw materials during drainage on the cylinder, thus ensuring that the final properties of
30 the sheet remain consistent. Overall retention is defined as the ratio of amount retained in the sheet to amount added to the stock.

In accordance with the present invention, one can employ a flat-wire fourdrinier paper machine, a single-cylinder wet-board and felt-making machine, two-

cylinder wet board and felt-making machine, or multiple-cylinder flat wire and felt-making system to form the sheet. This machine enables the production of a sheet thick enough to constitute the entire PWB core, eliminating the necessity for ply-to-ply lamination often associated with the production of PWB core stock. Using this machine, the thickness of the sheet produced can be varied to suit the needs of specific PWB applications. In some cases, if the application demands it, PWB core stock material in accordance with the present invention can be formed in other ways, such as manually in apparatus designed for decorative papermaking.

A single-cylinder wet-board-making machine is illustrated in **Figure 1**. It comprises a wire-mesh-covered cylinder mold **40**, free to revolve in a vat **42** bounded by a "circle" **44**. The vat **40** as shown is a direct-flow type; the direction of water flow is indicated by arrows. In the direct-flow vat **40**, an overflow is maintained over an adjustable control dam **46**, with vat overflow liquid and vat filtrate returning, with added stock, to a fan pump suction for recirculation to the vat entrance.

In operation, as the cylinder mold **40** revolves partially submerged in the vat **42**, water containing stock material passes through the face of the cylinder mold **40** under static head and out at its ends, leaving stock material as a web **50** on the face of the cylinder mold **40**. This continuously forming wet web **50** is picked up (or couched) from the top of the cylinder mold **40** by a traveling felt **52** pressed into contact by a couch roll **54**. The web **50** is carried by the felt **52** to a making roll nip **55** formed by a making roll **57** and a drive roll **58**.

The endless felt **52** as shown in **Figure 1** is draped around various rolls of the machine. The felt **52** travels downward from the making-roll nip **55** and around felt-carrying rolls **61** and **62**, a felt tension roll (or stretch roll) **64** and a wormed whipper roll **65**. Then it travels upward past a felt shower **72**, a revolving whipper **74**, a second felt shower **76**, over a turning roll **78** at which point its travel becomes horizontal, and over a felt cleaning and drying suction box **80**. Then the felt **52** contacts the up-turning web **50** on the cylinder mold **40**, at which point the felt **52** picks up the web **50**, and travels around the couch roll **54**, over a felt guide roll **56** and a web-drying suction box **59**, and finally back to the making roll nip **55**.

As the felt carrying the thin wet sheet passes into the nip formed by the making roll and the drive roll, the sheet is wound up on the making roll. The making roll is known as an accumulator or top press roll on some machines. When a

desired thickness is reached, as determined by the number of windings allowed on the making roll, the now-multilayered composite sheet is cut and removed from the making roll.

5 Finishing the sheet. At this point the sheet may be subjected to wet-pressing. Primary objectives of wet-pressing are to remove water from the sheet and to consolidate the web. Wet-pressing also provides surface smoothness and reduces bulk. Wet-pressing may be omitted if the particular application requires a low density or if the material is not highly saturated with water. Wet-pressing is accomplished by
10 interleaving wet PWB core stock sheets with woven synthetic sheets that provide a mechanism for water movement from the center region of the sheets to their edges. A stack of interleaved sheets is placed in a large hydraulic flat-platen press and is pressed under a substantial load for an extended period to allow for optimum water removal and consolidation. Typical wet-press loadings range from 200-300 psi for
15 from 10-45 minutes. Alternatively, where the system is appropriately configured, pressing can be conducted on-line.

After removal from the forming machine, and wet-pressing if that operation is employed, the sheets are placed into a dryer oven where residual water is removed by evaporation. Suitable oven types include continuous multizone dryers with
20 various heat sections and single-zone stationary convection ovens with variable temperature control. Temperature and drying times are selected in order to optimize water removal while insuring that the resin system does not cure beyond the B⁺ stage. Typical temperatures range from 220-280°F and typical oven dwell times range from 20-40 minutes. However, alternative drying systems, including different
25 time-temperature relationships, UV drying systems, vacuum drying canisters, heated canisters, microwave systems, and other drying systems practiced in the paperboard and related industries can also be used.

Surface and interior properties of the dried sheets may be improved by calendering. Calendering changes surface and interior properties of a sheet by
30 passing the web through one or more nips formed by a pair or pairs of smooth hard rolls. Calendering nip pressure is much higher than wet-press pressure; however, the time that any portion of the web spends in the nip is quite short, on the order of a fraction of a second. An objective is to press the sheet against the smooth surface

with sufficient force to deform the sheet plastically, giving it a smooth surface. Another objective is to remove entrapped air in the matrix by reducing void volume. Void volumes of materials of the present invention measured using a scanning electron microscope showed zero voids. Wetlaid webs are generally more variable
5 in profile and properties across their machine directions than they are in their machine directions. Calendering imparts a greater degree of machine direction/cross-direction uniformity to web profiles and to web properties including thickness. An uncalendered sheet of the present invention targeting a 0.426 inch thick dielectric core space and having a thickness in the range from 0.060-0.090
10 inches and an area density of from 0.135-0.170 grams per square centimeter can be reduced to a thickness in the range from 0.045 to 0.060 inches by a suitable calendering procedure.

PWB LAMINATES. Core stock material of the present invention can be used
15 to make printed wiring board laminates. For instance, referring to **Figure 2a**, a 4-layer CEM-1 grade laminate can be made by assembling a stack (or make-up assembly) **20** of lamina comprising, from bottom to top, a layer of epoxy-resin-saturated woven glass fabric **22**, a layer of core stock material **21**, a (second) layer of epoxy-resin-coated woven glass fabric **23**, and a layer of copper foil **24**. In an
20 alternative embodiment, not shown, a 5-layer laminate can be made by providing a layer of copper foil as a bottom and then proceeding as described in the preceding sentence. The stack **20** thus formed is pressed in a heated platen press, at pressures typically in the range from 200-1000 psi, causing the epoxy monomers to melt and to interact with the curing agent. Material manufactured in accordance with
25 the present invention can be used in systems that include a vacuum evacuation step or other conventional means to ensure the formation of laminate material while reducing volatile emissions during the lamination process.

A 3-dimensional cross-linked network is formed by the fully cured epoxy resins. At the same time, resin flow ensures that the core stock bonds to the glass
30 fabric and the glass fabric bonds to the copper foil. The result, illustrated in **Figure 2b**, is a CEM-1 grade printed wiring board composite **30** having a core of PWB core stock material **31** sandwiched between woven glass cloth outer layers **32** and **33**, the sandwich having a copper cladding **34**.

Paperboard sheets made in accordance with the present invention can also be used for making gaskets. For example, a paperboard sheet containing aramid fiber for extra toughness and heat-resistance can be formed to the desired thickness and B-staged. The epoxy resin fully cures in situ when exposed to operating
5 temperatures, creating a highly leak-resistant material.

Alternatively, paperboard sheets made in accordance with the present invention can be used to make molded three-dimensional objects. For example, a paperboard sheet containing one or more functional additives as described herein can be formed in a heated male/female mold and cured. The resulting structure can
10 be used in various applications to meet shape, structure, backing, electrical property, or other functional requirements.

EXAMPLES. The present invention is more fully illustrated by the following Examples, which demonstrate particular features of the invention. However, the
15 Examples are not to be construed as limiting the invention in any way, it being understood that numerous variations are possible without departing from the spirit and scope of the invention.

EXAMPLE 1 – wetlaid resin-containing board

EXAMPLE 1.a. This example employed a single-cylinder wet-board and felt-
20 making machine. Stock was prepared in a machine storage chest. Fresh water was added to a pulper, followed by 14.3 pounds of Mallette Abitibi bleached softwood Kraft pulp and 13.6 pounds of Mead Escanaba bleached hardwood Kraft pulp. The bone dry solid content of each pulp addition was 12.5 pounds, for a total of 25 pounds of cellulose fiber. The pulp was dispersed and then refined to 200 ml CSF.
25 The consistency was approximately 3½ % by weight at this point. The stock was returned to a pulper and 25 pounds of dry Dow Chemical D.E.R. 662UH epoxy powder was added. The epoxy was dispersed into the pulp dispersion and the pulp/epoxy dispersion was returned to the storage chest and diluted with more water. Then 1.43 pounds of liquid Huntsman XJT 504 amine (containing 100% solids) was
30 added, the pH was checked, and alum slurry was added to bring the pH to about 7. Then the mixture was pumped, together with a small amount of 0.1% by weight diluted Nalco 7524 cationic polymer, to the headbox and papermaking was carried

out in a conventional manner. An Amergel 200 defoamer was delivered as needed for foam control at the headbox. The product of this papermaking process was a paperboard comprising approximately 50% by weight epoxy resin dispersed in a matrix of 50% by weight cellulose fibers.

5 EXAMPLE 1.b. This example employed a single-cylinder wet-board and felt-making machine. Stock was prepared in a machine storage chest. Fresh water was added to a pulper, followed by 25 pounds (bone dry) of softwood pulp and hardwood pulp to provide a 50:50 mixture of softwood and hardwood cellulose fibers. The pulp was dispersed and refined. The consistency was approximately 3½ % by weight at
10 this point. The stock was returned to the pulper and 12.5 pounds of powdered EPON Resin 1183 and 22.73 pounds of Peninsula Polymers 6007 waterborne epoxy resin (containing 55 weight-% solids) was added to the pulper. The stock was dispersed and the pulp/epoxy dispersion was returned to the storage chest and diluted with more water. Then sufficient amounts of Huntsman XJT-504 amine
15 curing agent, in stoichiometric ratio to the total epoxy resin, was added to the chest and thoroughly mixed with the stock. The pH was checked and sufficient alum slurry was added to bring the pH to just below 7. Then the mixture was pumped, together with a small amount of 0.1% by weight diluted Nalco 7524 cationic polymer, to the headbox and papermaking was carried out in a conventional manner. An Amergel
20 200 defoamer was delivered as needed for foam control at the headbox. The product of this papermaking process was a paperboard comprising approximately 20% by weight brominated epoxy resin, 30% by weight unbrominated epoxy resin, 25% by weight softwood fibers, and 25% by weight hardwood fibers.

EXAMPLE 2 – wetlaid board containing water-borne resin and glass fiber

25 This example employed a single-cylinder wet-board and felt-making machine. Stock was prepared in a machine storage chest. Fresh water was added to a pulper, followed by 14.3 pounds of Mallette Abitibi bleached softwood Kraft pulp and 10.9 pounds of Mead Escanaba bleached hardwood Kraft pulp. The bone dry solid content of the softwood pulp was 12.5 pounds, and the bone dry solid content of the
30 hardwood pulp was 10 pounds, for a total of 22.5 pounds of cellulose fiber. The pulp was dispersed and then refined to 200 ml CSF. The consistency was approximately

3½ weight-% at this point. The stock was returned to a pulper and 18.75 pounds of dry Dow Chemical D.E.R. 662UH epoxy powder along with 2.5 pounds of Evanite 610 glass fiber was added. The epoxy and glass fiber were dispersed into the pulp dispersion and the pulp/epoxy/fiber dispersion was returned to the storage chest and
5 diluted with more water. Then 1.1 pounds of liquid Huntsman XJT-504 amine, 8.5 pounds of Peninsula Polymers 6007 water-borne epoxy resin (4.69 pounds of solids), and 4.5 pounds of Sancure 825 liquid urethane resin (1.56 pounds of solids) were added, the pH was checked, and alum slurry was added to bring the pH to about 6.5. Then the mixture was pumped, together with a small amount of 0.1% by
10 weight diluted Nalco 7524 cationic polymer, to the headbox and papermaking was carried out in a conventional manner. An Amergel 200 defoamer was delivered as needed for foam control at the headbox. The product of this papermaking process was a paperboard comprising approximately 50% by weight epoxy resin and 5% by weight glass fibers dispersed in a matrix of 45% by weight cellulose fibers.

15 **EXAMPLE 3 – wetlaid board containing resin, glass fiber, and clay**

This example employed a single-cylinder wet-board and felt-making machine. Stock was prepared in a machine storage chest. Fresh water was added to a pulper, followed by 11.5 pounds of Mallette Abitibi bleached softwood Kraft pulp and 8.2 pounds of Mead Escanaba bleached hardwood Kraft pulp. The bone dry solid
20 content of the softwood pulp was 10 pounds, and the bone dry solid content of the hardwood pulp was 7.5 pounds, for a total of 17.5 pounds of cellulose fiber. The pulp was dispersed and then refined to 200 ml CSF. The consistency was approximately 3½ weight-% at this point. The stock was returned to a pulper and 25.5 pounds of Ly-Resin 4 powder along with 4.5 pounds of Engelhard Translink 445
25 Clay was added. The resin and clay were dispersed into the pulp dispersion, and then 2.5 pounds of Evanite 610 glass fiber were dispersed into the pulp/resin/clay dispersion. The pulp/resin/clay/fiber dispersion was returned to the storage chest and diluted with more water. Then the mixture was pumped, together with a small amount of 0.1% by weight diluted Nalco 7524 cationic polymer, to the headbox and
30 papermaking was carried out in a conventional manner. An Amergel 200 defoamer was delivered as needed for foam control at the headbox. The product of this papermaking process was a paperboard comprising approximately 51% by weight

resin, 9% by weight clay, and 5% by weight glass fibers dispersed in a matrix of 35% by weight cellulose fibers.

EXAMPLE 4 – wetlaid board containing resin, glass fiber, microspheres, and Sb_2O_3

This example employed a single-cylinder wet-board and felt-making machine.

5 Stock was prepared in a machine storage chest. Fresh water was added to the chest, followed by 11.18 bone dry solid pounds of Mallette Abitibi bleached softwood Kraft pulp and 3.73 bone dry solid pounds of Jarilptus bleached Eucalyptus Kraft pulp, for a total of 14.92 pounds of cellulose fiber. The pulp was dispersed and then refined to 200 ml CSF. The consistency was approximately 3½ weight-% at this

10 point. The stock was returned to a pulper and 27.5 pounds of dry Ly-Resin 5 powder along with 1.44 pounds of flame retardant antimony trioxide powder was added. The resin and oxide powders were dispersed into the pulp dispersion, and then 2.25 pounds of Evanite 610 glass fiber and 2.25 pound of Minnesota Mining & Manufacturing K46 glass microspheres were dispersed into the pulp/resin/oxide

15 dispersion. The dispersed stock was returned to the storage chest and diluted with more water. The mixture was pumped to the headbox together with a small amount of 0.1% by weight diluted Nalco 7524 cationic polymer, and papermaking was carried out in a conventional manner. An Amergel 200 defoamer is delivered as needed for foam control at the headbox. The product of this papermaking process is

20 a paperboard comprising epoxy resin, glass fibers, glass microspheres, and flame retardant filler dispersed in a matrix comprising cellulose fibers.

EXAMPLE 5 – printed wiring board

25 A printed wiring board laminate is made by assembling a stack of lamina comprising, from bottom to top, a layer of 0.007-inch-thick epoxy-resin-coated glass fabric, a layer of nominal 0.04-inch-thick core stock material, produced in accordance with EXAMPLE 4, another layer of 0.007-inch-thick epoxy-resin-coated glass fabric, and a layer of one-ounce-per-square-foot copper foil. The glass fabric is a woven

30 fabric that has been treated with conventional saturation resin, Shell EPON 1124-A-80 epoxy resin (a brominated difunctional epoxy resin: 80 weight-% solids in

acetone solution). The stack thus formed is pressed for 60 minutes in a platen press that has been preheated to 340°F. The pressure of the press is maintained at about 300 pounds per square inch. The platen press is equipped with a vacuum system, which is maintained at 15 torr to promote the removal of volatile materials during the epoxy curing process. After 30 minutes, the temperature and pressure are slowly reduced. The product of this process is a CEM-1 grade printed wiring board. The materials as manufactured in this process may be also manufactured by processes in which vacuum systems are not employed. The times given in the above description will vary with different manufacturing systems.

10

CORE STOCK ELECTRICAL PROPERTIES. Electrical properties of the core stock of EXAMPLE 1.b. were evaluated. The procedures followed were those of MIL-S-13949H, Amendment 2. These tests are conducted to determine the electrical and physical properties of the materials and to assess whether the materials conform to CEM-1 standards. Resistivity results in MEGOHMS-CM, were as follows: volume resistivity, after elevated temperature, was $7.16\text{E}+07$; volume resistivity, after temperature/humidity, was $2.21\text{E}+09$; surface resistivity, after elevated temperature, was $2.91\text{E}+05$; and surface resistivity, after temperature/humidity, was $3.73\text{E}+06$. Dielectric breakdown (average for six samples) was 56.5 kilovolts. Permittivity (average for six samples) was 4.58. Loss tangent (average for six samples) was 0.026.

15

20

PWB ELECTRICAL PROPERTIES. Electrical properties of various PWB boards made with core stock of the present invention were evaluated.

25

Core stock was prepared by the procedure followed in EXAMPLE 3. Various blends of Mallette Abitibi bleached softwood Kraft pulp and Mead Escanaba bleached hardwood Kraft pulp were used. The resin system used comprised 86 weight-% EPON Resin 2002, 10 weight-% brominated diphenyl ether, and 4 weight-% EPI-CURE P108. The glass fiber used was Evanite 411. The clay used was Translink 445. Core stock was prepared from the formulations shown in Table 1:

30

Table 1 – CORE STOCK FORMULATIONS					
Formulation ID	Component Weight-Percent				
	<u>Cellulose type</u>		Resin system	Glass fiber	Clay
	Softwood	Hardwood			
708	17.5	14	58.5	3.5	6.5
709	15	12	63	3	7
710	10	12.5	67.5	2.5	7.5

This core stock was made into 5-layer PWB laminates by the procedure outlined above. Electrical properties of the PWB laminates so-produced were tested following NEMA LI-1 1989 procedures. These tests are conducted to determine the electrical and physical properties of the materials and to assess whether the materials conform to CEM-1 standards. The results, for tests after temperature/humidity, are reported in the Tables that follow:

Table 2 – VOLUME RESISTIVITY			
Lot Number	Sample	Test Results	MEGOHMS-CM
708L3	A	PASS	2.34E+07
708L3	B	PASS	1.92E+07
708L3	C	PASS	2.90E+07
708L4	A	PASS	1.90E+07
708L4	B	PASS	2.00E+07
708L4	C	PASS	2.81E+07
709N6	A	PASS	3.35E+07
709N6	B	PASS	2.59E+07
709N6	C	PASS	2.24E+07
710N5	A	PASS	9.38E+07
710N5	B	PASS	2.31E+08
710N5	C	PASS	6.40E+07
710N9	A	PASS	1.32E+07
710N9	B	PASS	1.20E+08
710N9	C	PASS	2.59E+08
710N10	A	PASS	2.82E+07
710N10	B	PASS	3.35E+07
710N10	C	PASS	2.52E+07

Table 3 – SURFACE RESISTIVITY

Lot Number	Sample	Test Results	MEGOHMS-CM
708L3	A	PASS	7.92E+07
708L3	B	PASS	1.91E+07
708L3	C	PASS	1.41E+07
708L4	A	PASS	5.09E+06
708L4	B	PASS	8.85E+06
708L4	C	PASS	7.35E+06
709N6	A	PASS	5.65E+06
709N6	B	PASS	6.90E+06
709N6	C	PASS	3.84E+06
710N5	A	PASS	1.43E+07
710N5	B	PASS	3.95E+06
710N5	C	PASS	5.65E+06
710N9	A	PASS	9.08E+06
710N9	B	PASS	1.78E+06
710N9	C	PASS	1.87E+07
710N10	A	PASS	1.66E+07
710N10	B	PASS	1.35E+07
710N10	C	PASS	1.27E+07

Table 4 – PERMITTIVITY

Lot Number	Sample	Test Results	Score
708L3	A	PASS	4.82
708L3	B	PASS	4.84
708L3	C	PASS	4.85
708L4	A	PASS	4.90
708L4	B	PASS	4.88
708L4	C	PASS	4.86
709N6	A	PASS	4.68
709N6	B	PASS	4.64
709N6	C	PASS	4.66
710N5	A	PASS	4.59
710N5	B	PASS	4.60
710N5	C	PASS	4.58
710N9	A	PASS	4.78
710N9	B	PASS	4.75
710N9	C	PASS	4.74
710N10	A	PASS	4.65
710N10	B	PASS	4.63
710N10	C	PASS	4.65

Table 5 – LOSS TANGENT			
Lot Number	Sample	Test Results	Score
708L3	A	PASS	0.032
708L3	B	PASS	0.033
708L3	C	PASS	0.033
708L4	A	PASS	0.034
708L4	B	PASS	0.034
708L4	C	PASS	0.033
709N6	A	PASS	0.033
709N6	B	PASS	0.030
709N6	C	PASS	0.029
710N5	A	PASS	0.031
710N5	B	PASS	0.030
710N5	C	PASS	0.030
710N9	A	PASS	0.032
710N9	B	PASS	0.031
710N9	C	PASS	0.031
710N10	A	PASS	0.031
710N10	B	PASS	0.030
710N10	C	PASS	0.030

BENEFITS. Among the benefits of the process of the present invention is the substantial reduction, relative to post-formation resin-impregnation processes, in the amount of organic solvents used. Another benefit is the flexibility which the process provides, inasmuch as it facilitates adjustment of physical as well as electrical properties. As discussed above, electrical properties are adjusted by the nature and amounts of functional additives incorporated into the core stock materials being produced. Physical properties of the sheet, such as density, dimensional stability, and thermal stability, likewise can easily be tailored as each PWB application demands, simply by adjusting processing parameters. Still another benefit is the ability to produce a sheet thick enough to constitute an entire PWB core, eliminating the necessity for ply-to-ply lamination often associated with the production of PWB core stock.

Among the benefits of products of the present invention are their improved electrical properties, including lower dielectric constant and dissipation factor, and their improved physical properties, including greater stiffness.

While there have been described and illustrated various specific embodiments of the invention, it will be clear that variations in the details of the embodiments specifically illustrated and described may be made without departing from the true spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A process for the manufacture of printed wiring board core stock material that comprises the steps
 - (a) forming a dispersion of cellulose fibers in water,
 - (b) adding a resin system comprising epoxy resin monomer and curing agent, in stoichiometric ratio, to said dispersion of cellulose fibers to form an aqueous mixture comprising a solids content of from about 65 weight-% to about 25 weight-% of cellulose fibers and from about 35 weight-% to about 75 weight-% of said resin system, and
 - (c) forming said mixture into a paperboard sheet.
2. The process of claim 1, wherein said curing agent is retained within said paperboard sheet and wherein said curing agent reacts substantially completely to cross-link said epoxy resin monomer when said paperboard sheet is maintained at a temperature of approximately 340°F for 30-60 minutes.
3. The process of claim 1, wherein the curing agent and the resin monomer are added separately to the dispersion of cellulose fibers.
4. The process of claim 1, wherein the curing agent and the resin monomer are melt-compounded together prior to their addition to the dispersion of cellulose fibers.
5. The process of claim 1, wherein said curing agent is dicyandiamide.
6. The process of claim 1, wherein said curing agent is an amine curing agent and wherein steps (b) and (c) are separated by a step (b2) which comprises adding a neutralizing agent to the mixture formed in step (b) to reduce the pH thereof to neutral or slightly acidic.
7. The process of claim 1, wherein step (a) additionally comprises adding functional additives having a dielectric constant and dissipation factor lower than that of said cellulose fibers to said dispersion of cellulose fibers in water.
8. The process of claim 7, wherein said functional additives are selected from the group consisting of glass fibers, aramid fibers, aramid powders, glass microbubbles, ceramic fibers, ceramic microbubbles, and clay.

9. The process of claim 1, additionally comprising the step
(d) drying said paperboard sheet without substantial cross-linking of said epoxy resin monomers and calendering the dried paperboard so-formed to form B-stage printed wiring board core stock material.
10. The product of the process of claim 1.
11. The product of the process of claim 9.
12. A paperboard material suitable for use as printed wiring board core stock comprising from about 25 weight-% to about 65 weight-% cellulose fibers forming a cellulose matrix, and having substantially evenly distributed throughout said matrix from about 75 weight-% to about 35 weight-% of a resin system comprising an epoxy resin and a curing agent.
13. The printed wiring board core stock material of claim 12, wherein said cellulose fibers comprise a mixture of softwood and hardwood fibers.
14. The printed wiring board core stock material of claim 13, comprising about 26 weight-% softwood fibers, about 8½ weight-% hardwood fibers, about 5 weight-% glass fibers, about 55 weight-% of said resin system, and about 5½ weight-% antimony trioxide.
15. The printed wiring board core stock material of claim 12, wherein said resin system comprises components that are brominated to a degree sufficient to impart flame retardant properties to said core stock material.
16. The printed wiring board core stock material of claim 12, wherein said curing agent is dicyandiamide or an amine having a number average molecular weight of at least 100 and an amine functionality of at least 3.
17. The printed wiring board core stock material of claim 12, formed to B-stage.
18. A printed wiring board core stock material comprising from about 25 weight-% to about 65 weight-% cellulose fibers, from about 75 weight-% to about 35 weight-% of a resin system comprising an epoxy resin and a curing agent, and from about 2 weight-% to about 20 weight-% of a functional additive having a dielectric constant and dissipation factor lower than that of said cellulose fibers.

19. The printed wiring board core stock material of claim 18, wherein said functional additive is selected from the group consisting of glass fibers, glass microbubbles, and clay.

20. The printed wiring board core stock material of claim 18, comprising about 15-20 weight-% softwood fibers, about 12-16 weight-% hardwood fibers, about 56-63 weight-% of said resin system, from 0 to about 4 weight-% glass fibers, and about 6-7 weight-% silane-coated calcined kaolin.

21. The printed wiring board core stock material of claim 18, comprising about 23 weight-% softwood fibers, about 8 weight-% hardwood fibers, about 57 weight-% of a resin system comprising an epoxy resin and a dicyandiamide curing agent, about 4½ weight-% glass fibers, about 4½ weight-% glass microspheres, and about 3 weight-% antimony trioxide.

22. The printed wiring board core stock material of claim 18, formed to B-stage.

23. In a printed wiring board composite comprising a core, the improvement comprising forming said core of core stock material as defined in claim 11.

24. In a printed wiring board composite comprising a core, the improvement comprising forming said core of core stock material as defined in claim 17.

25. In a printed wiring board composite comprising a core, the improvement comprising forming said core of core stock material as defined in claim 22.

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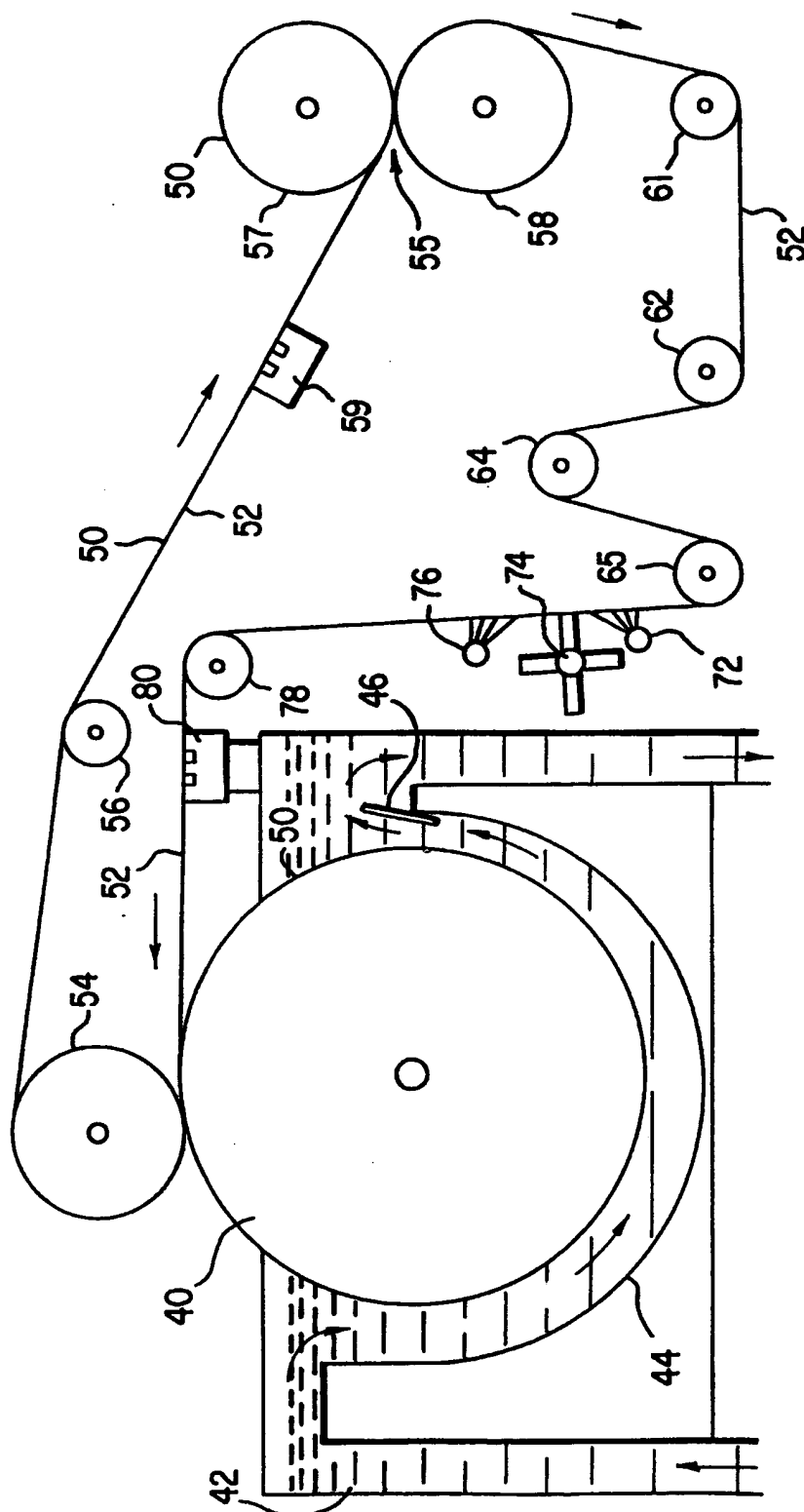


FIG. 1

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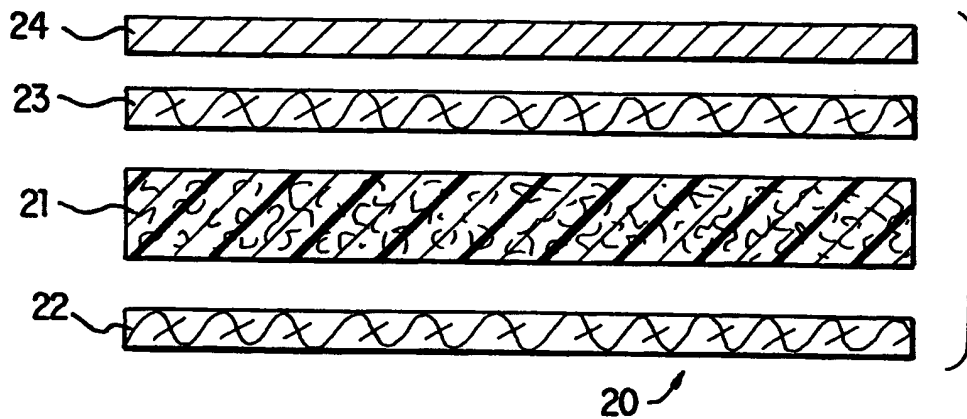


FIG. 2a

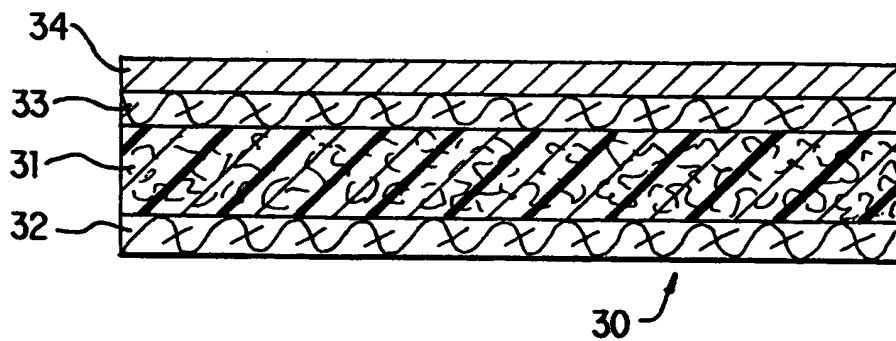


FIG. 2b

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/05138

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01B 3/00, 3/40

US CL :162/138, 156, 157.2, 158, 164.3, 164.6, 168.6

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/138, 156, 157.2, 158, 164.3, 164.6, 168.6; 174/17LF; 336/94

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,931,027 A (SADLER et al) 06 January 1976, col. 3, lines 16-20 and 57; col. 4, lines 35-43.	1-25
A	US 5,160,582 A (TAKAHASHI) 03 November 1992, col. 2, lines 42-44; col. 4, lines 54-59; col. 10, lines 48.	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 JUNE 1999

Date of mailing of the international search report

14 JUN 1999

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